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Carbon: Occurrence of Linear Forms in Natural Graphite

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15 April 1977

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This technical report has been reviewed and is approved for publication.

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FOR THE COMMANDER

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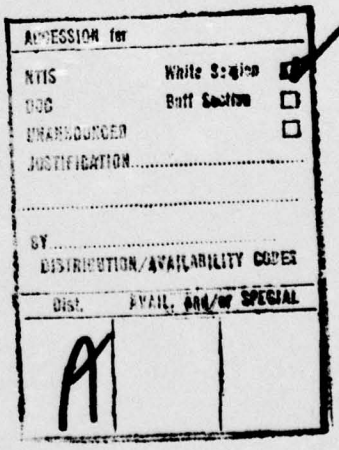

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A study of several natural carbon formations, from geographical locations ranging from Celyon to California, revealed that the carbons contain small amounts of linear carbon forms, e.g., chaoite, α carbyne, and β carbyne. The results indicate that these "rare" carbon forms have worldwide distribution and, as with diamond, are prevented from tranformation to graphite by a high kinetic barrier.

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PREFACE

C. H. Hills helped with the x-ray work, E. S. Watts the electron diffraction, N. Marquez the ion probe, A. L. Palyo the scanning electron microscopy, and M. E. Neudorffer the collection and preparation of the samples. The author gratefully acknowlwdges these coworkers for their assistance.

CARBON: OCCURRENCE OF LINEAR FORMS IN NATURAL GRAPHITE

Heretofore the linear carbon forms were believed to be rare forms found only in meteorites or meteorite craters or produced in trace quantities under unusual laboratory conditions. However, a study of natural carbon deposits indicates that one or more of these carbon forms commonly occur over a very wide geographic area.

Since these carbon forms are not well known, background on their properties is necessary. Each crystal form of carbon gives a characteristic negative-ion spectrum under conditions that prevail in an ion microprobe.[1,2] Because these phenomena were used extensively in the study of the linear carbon forms,[3,4,5,6] graphite from various natural sources was studied to check the universality of the method and to improve the accuracy of the graphite reference spectrum.

Another characteristic of the carbon forms was revealed by studying the etch patterns produced by the ion microprobe beam with a scanning electron microscope (SEM). In diamond and graphite (both in the a and c directions), the etch pattern is a smooth, essentially featureless, depression. The linear carbon forms and lonsdaleite etch into a variety of patterns such as pinnacles, sharp steps, and rounded steps. Although the detailed association between the patterns and carbon forms is far from established, the patterns are useful. At present, eight linear forms can be distinguished by their a_o values. Unfortunately, a_o and c_o are known for only chaoite, α and β carbyne,

and carbon VI and VII. Therefore, positive identification of all the linear forms is not possible at present. A few of these forms are very hard; Chaoite, for example, is harder than B_4C, which is a superhard material· others are as soft or softer than graphite. For the hexagonal carbon forms, there is a correlation between the etch pattern and the hardness. The soft forms show smooth shallow depressions; the hard forms show deep holes with the characteristic patterns on the walls and bottom. The hard forms also have a higher sputtering rate.

The first crystals studied were obtained from coarse crystalline marble from a quarry in Ticonderoga, New York. The crystals were removed from the marble with hydrochloric acid and subsequently washed in distilled water. They were analyzed with ARL ion microprobe mass analyzer (IMMA) Model 101000 in both the positive- and negative-ion secondaries from the samples. The positive-ion spectrum indicated very few impurities in trace amounts; in the negative-ion spectrum, the results differed, depending on the location probed. At A in Fig. 1(a), a typical graphite spectrum was obtained. At B, the spectrum is characteristic of the linear carbon forms. The probe holes produced at these locations were examined with an SEM. The hole at A is the typical featureless depression characteristic of graphite and is in agreement with the C_n^- ion spectrum obtained at that point. The probe hole produced at B had a complex etch pattern, Fig. 1(b). In this case, the ion beam just grazed the vertical face of a growth step on the crystal surface. It is evident that the crystal is not a single form but consists of layers of different carbon forms. The first layer is a very thin layer of a linear form.

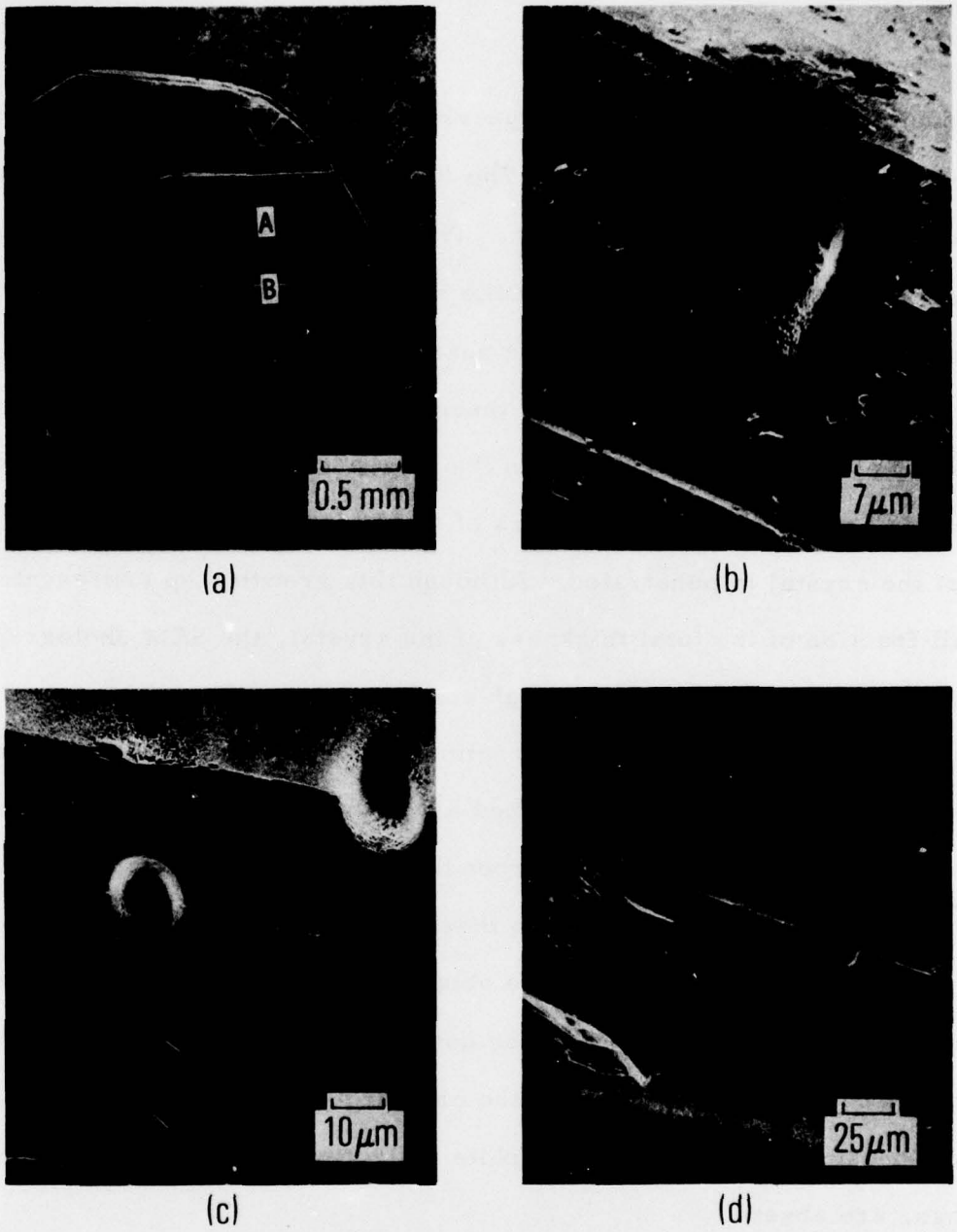

Fig. 1. Carbon Crystals. (a) Carbon crystal from Ticonderoga marble; (b) Same crystal as in (a) showing magnified image of ion probe hole at B; (c) Carbon crystal from Santa Rosa Mountains marble showing probe holes on a prism face; (d) Same crystal as in (c) showing mechanically damaged edge.

The second is a thin layer of what appears to be graphite. The third layer is one of the linear carbon forms. The fourth layer may be graphite, as indicated by the smooth etch surface. The fifth, sixth, and seventh are linear forms. The fifth and seventh are of the same form, but the sixth is different. The step edges of the sixth layer are sharper than those of the adjacent layers. More important, it is brighter and, therefore, gives a higher yield of secondary electrons than the form in the adjacent layers. The eighth layer appears to be graphite. Other layers of linear forms appear as the major body of the crystal is penetrated. Although this growth step represents only a small fraction of the total thickness of the crystal, the SEM photograph indicated that there was a high enough concentration of linear forms to produce lines or spots on an x-ray diffraction (XRD) pattern. This prediction was correct, and the d-values obtained are shown in Table 1. The crystal was rotated about an axis nearly perpendicular to the c-axis in order to minimize orientation effects. From these data, it is evident that there are many more reflections than would be obtained from graphite. Since the IMMA showed a very low impurity level, the nongraphite reflections must result from other carbon forms. Indeed, the crystal probably contains very little graphite because two prominent graphite reflections, the 1.23- and 1.16-Å spacings, are absent.

The crystal was mounted and sliced by means of an ultramicrotome in the hope that high-energy electron diffraction (HEED) could be performed at suitable places across the slice, and thereby the layers could be identified unambiguously. Unfortunately, the soft layers were crushed, and the hard

Table 1. X-ray diffraction data from carbon crystals obtained from Ticonderoga and Santa Rosa Mountain marble

Ticonderoga		Santa Rosa	
Observed d, Å	Relative[a] Intensity	Observed d, Å	Relative Intensity
6.607	S	3.818	S
4.133	S	3.453	S
3.648	M	3.069	M
3.376	VS	2.659	M
2.122	M	2.132	S
2.014	M	2.032	S
1.793	W	1.804	S
1.675	S	1.549	S
1.544	W	1.321	M
1.519	W	1.290	W
1.315	VVW	1.234	W
1.137	VVW	1.158	S
1.119	M	1.137	M
1.060	VVW	1.055	W
1.047	VW		
1.010	VVW		
0.9906	VW		
0.9584	VW		
0.8739	W		
0.8384	M		

[a]Intensities are graded in the order of increasing intensity as follows: VVW - VW - W - M - S - VS

layers crumbled, destroying the relationship between the layers and the diffraction patterns. However, the HEED results overlapped the x-ray data rather well; and, as usual, each technique produced reflections that the other did not. On the basis of the negative ion spectra and the diffraction data, the following tentative assignments were made: the fifth and seventh layers are β carbyne; and the sixth is α carbyne or chaoite.

Ten crystals from Ticonderoga marble were studied. Three or four of them consisted of graphite only; the rest had a layered structure and linear forms. However, this was a poor sampling of a fairly large geological formation and may not be representative of the entire formation.

A carbon crystal obtained from a graphitic marble from the Santa Rosa Mountains, Imperial County, California, also was analyzed. Again, the positive-ion spectra showed very few impurities in trace amounts, and the negative ion spectrum depended on the location probed. Several probe holes on a prism face (hexagonal crystal) are shown in Fig. 1(c). The layer structure is evident, and the etch patterns indicate that about two-thirds of the crystal thickness is of a soft form and one-third of the thickness is a hard form. This conclusion is supported by the appearance of a mechanically damaged edge, Fig. 1(d). The region showing the smooth etch pattern deformed as a soft material, and in the region showing the deep holes with clear etch patterns there is evidence of brittle fracture.

The x-ray diffraction results are shown in Table 1. Many nongraphite reflections were observed. Note that the strong reflection at 3.45 Å occurs at a d-value that is high for a well-formed graphite crystal and that the

reflection at 1.234 Å is weak, whereas the one at 1.158 Å is strong. In graphite, these reflections are of nearly equal intensity. None of the carbon negative-ion spectra indicated the presence of graphite. Therefore, this crystal contains no graphite, even though a superficial inspection of the XRD data suggests that the crystal is an impure graphite crystal. Another indication that the crystal is not graphite is its shape. Graphite crystals have hexagonal symmetry, whereas this crystal has trigonal symmetry, which is the symmetry seen most often in crystals of the linear carbon forms.

Similar results were obtained for carbon samples obtained from Ceylon; Fossil Canyon; the Coyote Mountains, Imperial County, California; Pacoima Canyon, the San Gabriel Mountains, California; and Coon Creek Canyon, the San Bernardino Mountains, California. Pacoima Canyon material was fractionated according to density. The fraction between 2.9 to 3.3 g/ml was a fairly pure fraction of a form tentatively designated at carbon VII. This study is continuing, and the final detailed results will be published later. At this time, the above findings suggest that the linear carbon forms can be found all over the world. As with diamond, they are thermodynamically unstable and have a kinetic barrier to transformation that allows them to exist for at least 60 million years.

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